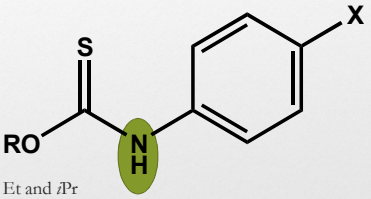
SUNWAY UNIVERSITY

Phosphane metal(I) thiolate complexes and their crystal structures

Yeo Chien Ing

Jeffrey Cheah Foundation

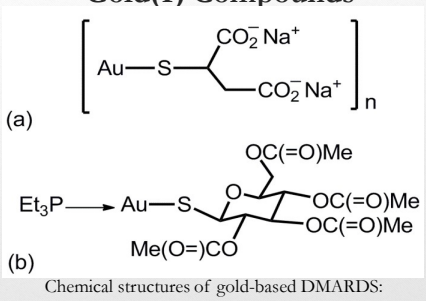
Thiocarbamide



R = Me, Et and *i*Pr

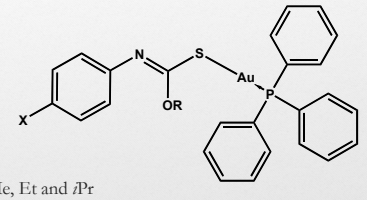
X = H and CH_3

Gold(I) Compounds



Chemical structures of gold-based DMARDS: (a) Myocrisin® and (b) Auranofin®

Triphenylphosphanegold(I) Carbonimidothioates



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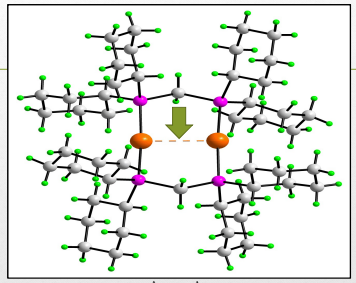
Gold(I) Compounds



Au - - - Au

Aurophilic Interactions

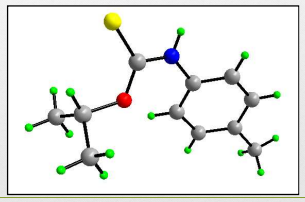
P.P.T. Tickink and J.-G. Kang, *Coord Chem Rev.*, 2009, **253**, 1627.

Triphenylphosphanegold(I) Carbonimidothioates

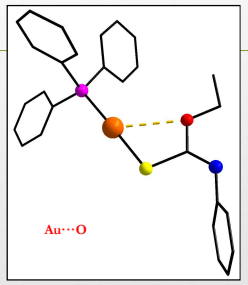
Molecule	Assignment	Chemical Shift (ppm)	
		Ligand	Metal Complexes
Thiocarbamide	^{1}H – N-**H**	~ 8.7	-
Triphenylphosphine	^{31}P – Ph_3**P**	-5.2	~ 38.0

*i*PrOC(=S)N(H)C_6H_4-4-Me

Bond	Bond length (Å)
C = S	1.6679 (19)
C – N	1.337 (2)

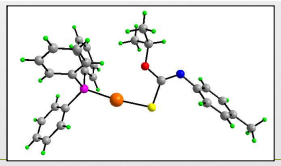


$Ph_3PAu[SC(OEt)=NPh]$

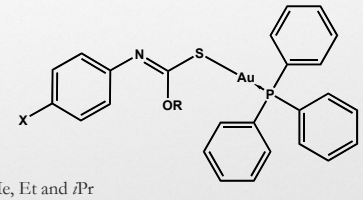


$Ph_3PAu[SC(O$*i*$Pr)=N(p\text{-tolyl})]$

Bond	Bond length (Å)
Au – P	2.2561 (7)
Au – S	2.3171 (7)
C – S	1.776 (3)
C = N	1.269 (4)



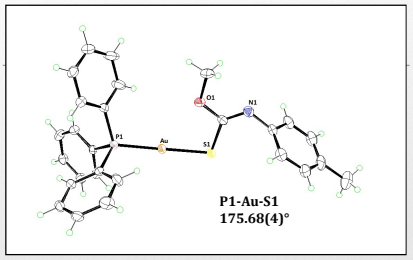
Triphenylphosphanegold(I) Carbonimidothioates



R = Me, Et and *i*Pr

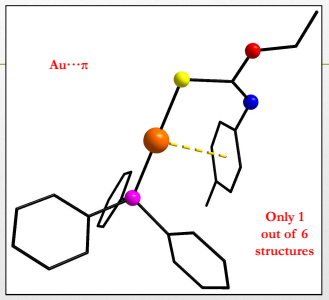
X = H and CH_3

$Ph_3PAu[SC(OMe)=N(p\text{-tolyl})]$

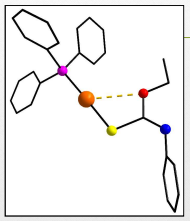


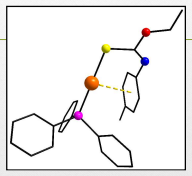
Molecular structures of $Ph_3PAu\{SC(OMe)=NC_6H_4CH_3\text{-}p\}$. Displacement ellipsoids are shown at the 50% probability level.

$Ph_3PAu[SC(OEt)=N(p\text{-tolyl})]$



Au···O versus Au···π





Au···π is more stable by ca 12 kcal/mol

At rotation angles = 0 and 360 ° about the C–S bond, Au···π is featured while at 180 °, Au···O is observed

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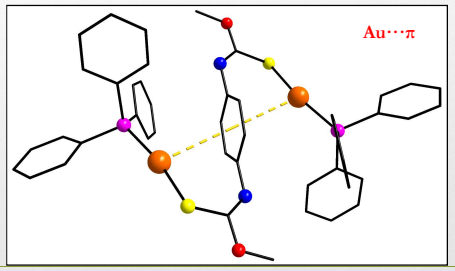
Binuclear Phosphanegold(I) Carbonimidothioates



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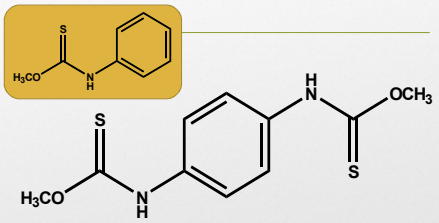
Bipodal Thiocarbamide



Chemical structure of 1,4-[MeOC(=S)N(H)]$_2$C$_6$H$_4$

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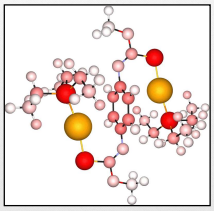
Binuclear Phosphanegold(I) Carbonimidothioates



Two intramolecular Au···π(aryl) interactions

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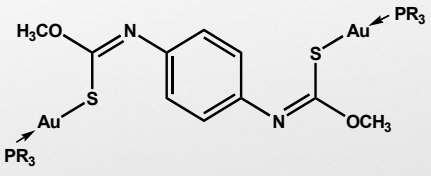
Binuclear Phosphanegold(I) Carbonimidothioates



R = Et, Ph and Cy

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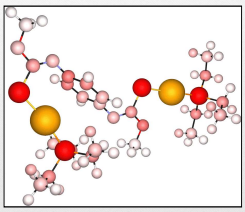
Binuclear Phosphanegold(I) Carbonimidothioates



12.2 kcal mol^{-1}

One Au···π(aryl) interaction and one Au···O interaction

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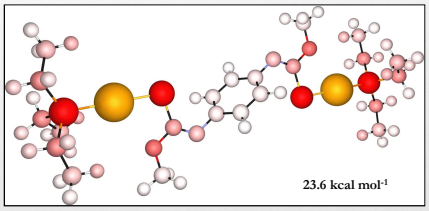
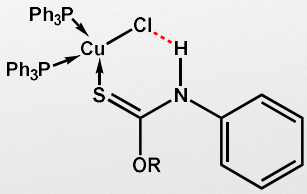
Binuclear Phosphanegold(I) Carbonimidothioates



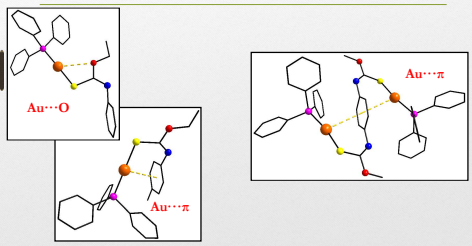
Two Au···O interactions

Formation of N-H…Cl

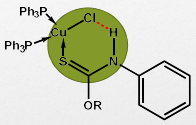


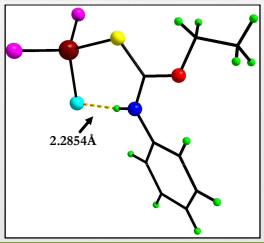
R = Me, Et and *i*Pr

Mono- vs Bi-nuclear Phosphanegold(I) Carbonimidothioates



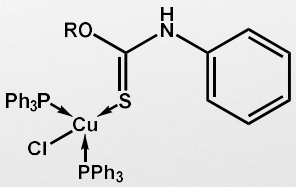
Six Membered Quasi Chelate Ring (CuCl…HNCS)





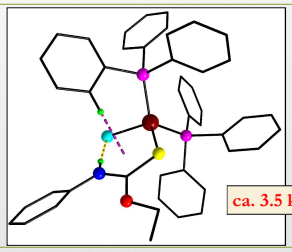
R = Me, Et and *i*Pr

$(Ph_3P)_2Cu[ROC(=S)N(H)Ph]Cl$

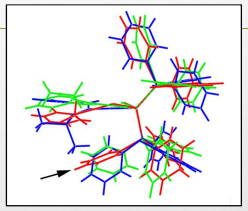


R = Me, Et and *i*Pr

C-H···π(quasi chelate ring)



$(Ph_3P)_2Cu[ROC(=S)N(H)Ph]Cl$



Overlay diagram of **Me** (red image), **Et** (green) and *i***Pr** (blue). The molecules have been superimposed so the P1-Cu-P2 atoms are overlapped. In this diagram, the inverted molecule of **Et** has been employed for a better fit.

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Acknowledgement

Special thanks to

Sunway University for the financial support

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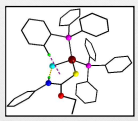
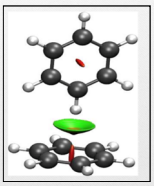
C-H···π(quasi chelate ring)





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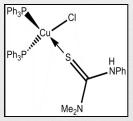

Chemical structure of the molecule subjected to DFT-D calculations (BP86-D/def2-TZVP)

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Thank You

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Summary

- Au…O interactions predominate in mononuclear gold(I) compounds.
- Au…π interactions in binuclear gold(I) compounds impart stabilisation to the structure.
- Copper(I) derivatives displayed arene-C-H···π(quasi-chelate ring) interactions with stabilisation energy of ca. 3.5 kcal mol^{-1}.

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